ENR based Vitrimers through Dynamic Boronic Ester Networks

Dissertation submitted to
Visvesvaraya National Institute of Technology, Nagpur
in partial fulfilment of the requirements for the award of
the degree

Master of Science

In

Chemistry

by

Nikita (MS23CHM011)

under the guidance of

Dr. Chayan Das

Department of Chemistry
Visvesvaraya National Institute of Technology
Nagpur 440 010 (India)
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Department of Chemistry
Visvesvaraya National Institute of Technology, Nagpur

Declaration

I, Nikita, hereby declare that this dissertation titled "**ENR based Vitrimers through Dynamic Boronic Ester Networks**" is carried out by me in the Department of Chemistry of Visvesvaraya National Institute of Technology, Nagpur. The work is original and has not been submitted earlier whole or in part for the award of any degree/diploma at this or any other Institution / University.

Nikita (MS23CHM011)

Date:

Certificate

This to certify that the dissertation titled "**ENR based Vitrimers through Dynamic Boronic Ester Networks**" is submitted by **Nikita** in partial fulfilment of the requirements for the award of the degree of **Master of Science in Chemistry** VNIT Nagpur. The work is comprehensive, complete and fit for final evaluation.

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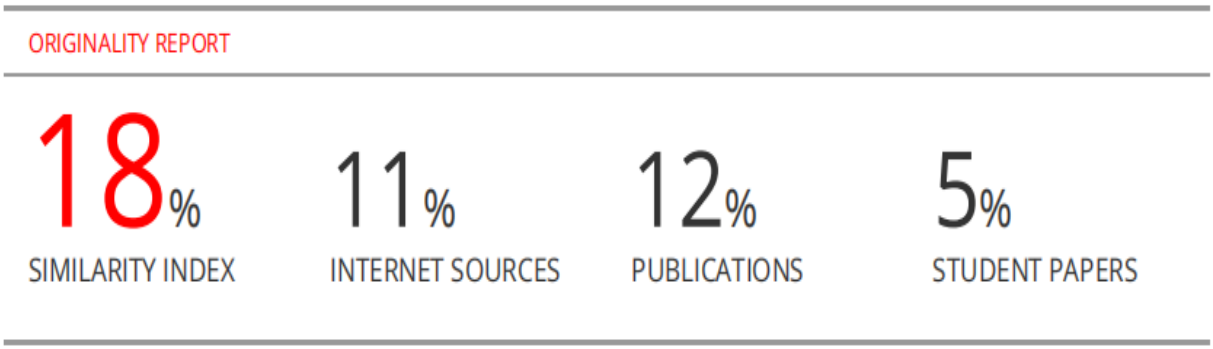

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Thank you all for making this journey a memorable and rewarding one!

Dedicated to my Guide
and
my beloved Parents

ENR based Vitrimers through Dynamic Boronic Ester Networks

Abstract:

Vitrimers represent a novel class of polymers, distinguished by their dynamic covalent networks. The presence of these dynamic bonds enables the fabrication of recyclable, self-healing materials that exhibit significant mechanical strength and thermal stability. In this study, epoxidized natural rubber (ENR-50), has been chemically cross-linked by boric acid via formation of reversible boronic ester linkages. Zinc acetate ($Zn(OAc)_2$) has been used, as a catalyst, to promote the dynamic bond exchange reactions. The resultant ENR-50 composites show improved mechanical and viscoelastic properties. The dynamic interactions between epoxy group of ENR-50 and hydroxyl group of boric acid reinforce the rubber matrix and maintain flexible nature as well. Crosslinking in ENR-50, via boronic is established by Fourier transform infrared spectroscopy (FTIR) and solid-state nuclear magnetic resonance (NMR) spectroscopy. The thermal and mechanical behaviour of the composites are studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and stress- strain study. Furthermore, dynamic mechanical analysis (DMA), and rheological studies have also been done. This study demonstrates potential of boric acid to construct covalent adaptable networks (CANs), offering a promising pathway toward sustainable polymer materials.

Keywords: vitrimer, dynamic covalent networks, recyclability, viscoelasticity

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LIST OF SYMBOLS/ ABBREVIATION

Symbols/ Abbreviation	Full form
NR	Natural Rubber
ENR	Epoxidized Natural Rubber
BA	Boric acid
FTIR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
UTM	Universal Testing Machine
DMA	Dynamic mechanical analysis
TGA	Thermogravimetric analysis
SEM	Scanning Electron Microscopy

CHAPTER 1:
INTRODUCTION

1.1 Introduction:

Thermoset polymers are widely acknowledged for their remarkable thermal stability, chemical resistance, and mechanical strength. These properties are attributed to their robust, three-dimensional covalent crosslinked networks. These characteristics, while advantageous for durability, render thermosets inherently non-reprocessable and non-recyclable, as they neither melt upon heating nor dissolve in solvents. Consequently, the disposal and reutilization of thermoset materials pose significant environmental and technical challenges, thereby contributing to the growing demand for sustainable polymer solutions.[1]

In response to these limitations, a novel class of materials known as vitrimers has emerged as a transformative development in polymer science. Vitrimers are covalently crosslinked polymers that incorporate dynamic covalent bonds capable of reversible exchange reactions. These exchanges enable the polymer network to undergo structural changes without compromising its structural integrity, facilitating reprocessing, reshaping, and even self-healing capabilities. The term "vitrimer," inspired by the Latin word vitrum (glass), reflects their ability to flow like a glass when heated, blending the reworkability of thermoplastics with the stability of thermosets.[2] This distinctive combination positions vitrimers as a pioneering material class with the potential to redefine polymer applications.

In order to comprehend the full significance of vitrimers, it is imperative to situate them within the broader context of polymeric materials, which are typically classified into three categories: thermoplastics, thermosets, and elastomers.[3] In contrast to thermoplastics, which are characterized by their ease of remolding yet exhibit a deficiency in thermal and mechanical robustness, and to traditional thermosets, which are notable for their durability but are non-recyclable, vitrimers employ dynamic covalent chemistry to achieve a harmonious integration of these properties. Elastomers, such as vulcanized rubbers utilized in industries such as the automotive and electronics sectors, encounter comparable recyclability challenges due to their stable crosslinked networks. By introducing reversible bond mechanisms, vitrimers offer a pathway to overcome these limitations, enhancing the sustainability of thermosets and elastomers.[4]

These advancements, based on the principles of dynamic covalent chemistry, extend beyond vitrimers to other materials, such as elastomers like natural rubber (NR) and its derivatives. Natural rubber, derived from the latex of Hevea brasiliensis, is a

cornerstone elastomer that is valued for its elasticity, tensile strength, and resilience. However, its susceptibility to oils and gases imposes limitations on its versatility. To address this, epoxidized natural rubber (ENR) has been developed through chemical modification, incorporating epoxy groups into the polymer backbone to enhance polarity. This modification has the potential to enhance ENR's compatibility with polar fillers, such as silica. Furthermore, it facilitates the integration of dynamic covalent bonds, aligning ENR's properties with those observed in vitrimers concerning their reprocessability. ENR is commercially available in grades such as ENR25 and ENR50, which vary in epoxy content. ENR finds application in a variety of fields, ranging from adhesives to automotive components, due to its adaptability and performance.[5]

Covalent adaptable networks (CANs), including vitrimers, leverage dynamic covalent bonds or strong supramolecular interactions to enable bond rearrangement and reprocessability in crosslinked polymer systems. CANs are classified into two distinct categories: dissociative and associative. Among these, associative CANs, also known as vitrimers, have the capacity to preserve crosslink density during topology rearrangement. The utilization of diverse exchange reactions enables the reprocessing of vitrimers at elevated temperatures, thereby enhancing their recyclability and sustainability. These properties expand the potential applications of vitrimers and enable the design of materials with superior performance and functionality.[6]

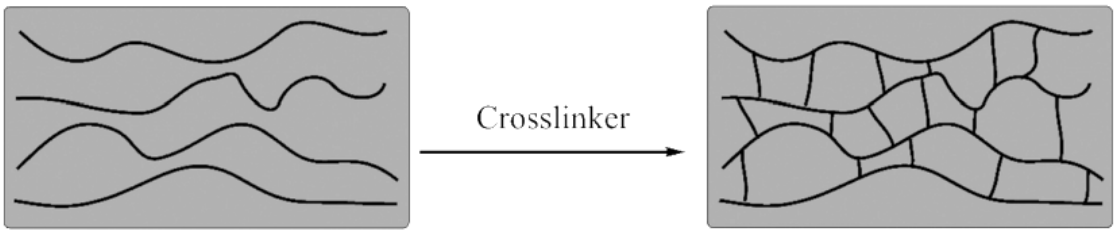
In order to realize the full potential of vitrimers in various industries, it is essential to possess a thorough understanding of their chemical composition, properties, advantages, and limitations. The ability to overcome challenges related to processing techniques and cost will be critical to achieving widespread adoption. The recyclability, durability, and versatility of vitrimers suggest a promising pathway toward sustainable polymer solutions, aligning with circular economy principles. Advancements in vitrimer technology have been achieved through the integration of said technology with functionalized elastomer materials, such as ENR.[7]

In the field of elastomers, crosslinking is a critical process that significantly enhances the mechanical and thermal characteristics of the material, thereby expanding its applications. The process of crosslinking involves the formation of covalent bonds between polymer chains, thereby converting elastomers from soft, viscous substances into resilient, elastic materials. This transformation offers numerous advantages, including enhanced elasticity, which enables rubber to regain its shape after

deformation.[8] It also increases strength, improving tensile properties and abrasion resistance. Furthermore, the transformation enhances thermal endurance, allowing performance at elevated temperatures. Additionally, it provides chemical resilience, making it ideal for harsh chemical environments. Other benefits include minimized creep and permanent deformation, ensuring long-term shape stability. Superior compression set, vital for seals and gaskets, is another advantage. Finally, the transformation improves resistance to aging and environmental factors, extending service life. These properties indicate that crosslinked elastomers are well-suited for applications that demand flexibility, toughness, and reliability under challenging conditions.[9]

1.2 Properties of cross-linked materials:

Crosslinking in the rubber matrix is essential for improving its mechanical and thermal properties, making it suitable for various applications. The process of crosslinking in the rubber matrix involves creating dynamic covalent bonds between polymer chains, which transform the elastomer into highly applicable material.[10]



Elastomer chains before crosslinking Cross linked elastomer chains

Figure 1.1: Crosslinking in elastomers

Below are some properties of crosslinked materials:

i) Improved Strength:

Crosslinking in the rubber matrix creates a three-dimensional network of bonds between polymer chains, significantly increasing the mechanical and thermal properties of material. This makes the rubber more durable and able to withstand high temperature and mechanical stress.

ii) Improved Elasticity:

Rubber, a sticky and malleable material, can be transformed into a more elastic one via Crosslinking. This allows the rubber matrix to return to its original shape after being stretched or deformed, which is essential for applications requiring flexibility and resilience. The dynamic nature of vitrimer bonds enables them to be reshaped, recycled or reprocessed.

iii) Chemical Resistance:

Crosslinking in rubber matrix makes the material more resistant to water, solvents, oils, and other chemicals.[12] Crosslinking in materials increases cross-linking density which improves resistance to corrosion and swelling in solvents. This property is vital for products like hoses, seals, and gaskets that must maintain integrity in harsh chemical environments.

iv) Thermal Stability:

Crosslinked rubber matrix exhibits enhanced thermal stability due to their network structure which provides improved heat resistance and improved glass transition temperature. This thermal stability is important for applications where the material is exposed to varying temperatures, such as in automotive, aerospace, electronics and industrial settings.

V) Reprocessability:

Crosslinking in rubber matrix reduces the tendency of rubber to deform permanently under compressive loads or after being stretched. This affirms that rubber products maintain their shape and functionality over time and stress.[13] Recyclable or reprocessable rubber matrix can be majorly used to make eco-friendly, lightweight and durable products.

1.3 Different Crosslinking Methods of Elastomer:

Cross-linking is a chemical process that forms bonds between distinct parts of a polymer chain in the matrix. This process increases the polymer's stiffness and longevity

(Figure 1.1). The cross-linking process has been shown to enhance the mechanical strength, viscoelasticity, stiffness, and longevity of the polymer. Without cross-links, polymer chains may slip under the external load, resulting in irreversible distortion. Cross-links, however, inhibit this slippage, thereby enabling the strained chains to recoil and revert to their original configuration once the stress is eliminated. These interconnections have been shown to have a significant impact on the material's mechanical performance. These materials are composed of extended polymer chains that are interconnected by irregular cross-links. The resulting cross-linked polymers exhibit enhanced stability and resistance to heat and mechanical stress.[14]

i) Sulphur Vulcanization:

In sulfur cross-linking, rubber is heated at 160^{o}C along with some ingredients like sulfur (primary cross-linking agent), accelerators (diphenylguanidine), activators (ZnO, stearic acid,), fillers (carbon black, silica, calcium carbonate), plasticizers (mineral oils, petroleum-based oils), antioxidants (BHT, diphenylamine) etc. these are used in various combinations and proportions to achieve the desired properties in the final rubber product, this process is known as sulfur vulcanization. This process is non-recyclable, non-self-healable and difficult to reprocess, also it can release harmful gases and toxic by-products, having some effective properties like increased elasticity, high tensile strength, high thermal stability, heat resistance, etc.[15]

ii)) Ultra-violet Radiation:

UV radiation actuates cross-linking in polymers, protecting fabric properties without adding chemical substances. This fast, cost-effective strategy guarantees less toxicity and can be performed at room temperature.[16] UV cross-linking is promising for creating custom-made polymers, illustrated in synthesizing hydrogels and cross-linking poly (vinyl liquor), advertising preferences over conventional strategies.

iii) Free-radical Polymerization:

Chemically cross-linked polymers are synthesized through suspension, emulsion, or scattering polymerization. These steady polymers can be degradable or non-

degradable. Free-radical polymerization makes polymers from acrylic corrosive and acrylate-based monomers, exhibiting flexibility in different applications.[17]

iv) Peroxide Curing:

Peroxide cross-linking is a widely used method to enhance polymer properties by forming covalent bonds between chains via free radical mechanisms. Unlike sulfur vulcanization, it offers superior heat resistance and stable mechanical properties. Organic peroxides decompose to generate free radicals, initiating cross-linking by abstracting hydrogen atoms and forming carbon-carbon bonds. Methods like the Engel process, Pont a 'Mousson, and Daoplas processes utilize peroxide breakdown to form carbon bonds in polyethylene. Alkyl peroxides are commonly used due to their high reactivity. These techniques enable cross-linking in various applications, improving material performance and durability. They are valuable in many industries.

2) Physical Cross-Linking:

Unlike chemical cross-linking, physical cross-linking is relatively weak and relies on secondary forces such as ionic interactions, hydrophobic forces, hydrogen bonding, stereo complexation, and supramolecular chemistry. Among physical cross-linking methods, ionic interaction is the strongest. The reversible nature of physical cross-linking allows for dynamic adjustments in material properties[18]. This characteristic makes physical cross-linking a versatile approach for various applications.

3) Biological Cross-Linking:

Biological cross-linking uses biomolecules like oligonucleotides and oppositely charged peptides to create cross-links. Specific oligonucleotides form cross-linked polymers that are insoluble in aqueous and organic solvents.[19] This approach is weaker than chemical cross-linking and reversible in respect to temperature and pH changes. Despite limitations, its unique properties make it suitable for specific uses. Further development is needed to overcome limitations and explore its potential in various fields, potentially leading to innovative applications.[20]

CHAPTER 2
LITERATURE REVIEW

The emergence of vitrimers has revolutionized the crosslinked matrix, offering new opportunities for creating high performance materials with tailored properties. This chapter presents a critical review of the current research areas on vitrimers, with a focus on their synthesis, properties, and applications.

1. A vitrimer composite utilizing polycarbonate and common cellulose paper was presented by Wei Zhao and his group, with extraordinary mechanical properties, thermal properties, and additional properties such as shape-memory and self-healing exhibited. This sustainable material was found to be recyclable, establishing it as a promising green solution.[21]

2. A family of biobased polyimine vitrimers was developed by Raymond Hajj and his research team, with dynamic behavior exhibited due to imine bonds formed between di- and trifunctional polyetheramines and a furan-based dialdehyde. It was found that cross-link density is directly proportional to relaxation time and activation energy. Control over relaxation properties was demonstrated through modification of the matrix properties alone, without the introduction of any catalyst.[22]

3. The self-healing mechanism in epoxidized natural rubber (ENR) with dicumyl peroxide and sulfur was investigated by James Boden and his co-researchers to provide convincing models of commercial rubber formulations. The effect of crosslinking on the self-healing efficiency of epoxidized natural rubber and natural rubber matrices was analyzed. A foundation was established by this work for the further improvement of ENR with the aim of evaluating self-healing ability for future applications.[23]

4. The incorporation of fillers into vitrimers was found by Amber M. Hubbard and her team to significantly enhance thermomechanical properties, creep resistance, and self-healing ability. By tailoring the filler composition, a new composite was designed with specific properties such as topology freezing temperature (Tv), high strength, and recyclability. This composite was made more attractive for various applications including actuators, strain sensors, and coatings.[24]

5. A covalent bond with boronic ester linkages was synthesized by Lingyun Huang and his team, empowering self-healing, shape memory, and recyclability in elastomers. Mechanical robustness, high stretchability, and ductile strength were imparted by this

method. Potential applications including flexible wearable devices and rubber-based vitrimer elastomers were suggested, offering a promising approach for developing sustainable and high-performance materials.[25]

6. A promising method for producing self-healing epoxidized natural rubber (ENR) materials was developed by Tamonwan Chantaramanee and his team using borax as a crosslinking agent. A dynamic crosslinked network formed through borate-ester and hydrogen bonds was shown to enable remarkable self-healing performance without external stimuli. High self-healing efficiency (>90%) at room temperature and excellent performance (>80%) after only 4 hours were exhibited by ENR with 10 phr borax. A practical approach for developing functional elastomers was offered by this study.[26]

7. A new method for assessing the heat generation of rubber compounds was introduced by C. Ajay and his research team using a rubber process analyzer (RPA). Thermal structure was measured by analyzing Tanδ under constant energy input, and a strong correlation with traditional methods was demonstrated. An efficient and accurate technique for evaluating heat generation and supporting the optimization of rubber compound structures was provided by this approach.[27]

8. The ring-opening reaction of epoxidized natural rubber (ENR) with acetic acid was examined by Rosniza Hamzah and her team using NMR, FTIR, TG/DTG, and DSC analyses. A 19.56% epoxy ring opening was observed, leading to the formation of hydroxyl groups and ester bonds. Changes in thermal properties and failure behavior of the modified ENR were reported.[28]

9. The crosslinking behavior of epoxidized natural rubber under high-energy radiation was examined by M.C. Senake Perera and his team, primarily through epoxy group ring opening. Crosslinking was observed both in vacuum and in air, with more pronounced effects under vacuum conditions. Minimal oxidation was observed in samples irradiated in air.[29]

10. The complexation chemistry of sodium borate (SB) with poly (vinyl alcohol) (PVA) and other polyols was studied by Steve W. Sinton using ^{11}B NMR spectroscopy. The cross-link structures in PVA/SB systems were identified, with two distinct cross-linking

complexes being distinguished. Correlations between NMR parameters and viscosity were explored.[30]

11. The vitrimer transition temperature (Tv) of dynamic covalent materials was illustrated by Amber M. Hubbard to be influenced not only by chemical structure but also by experimental parameters such as heating rate, applied force, and catalyst concentration. A kinetic model was developed to confirm the temperature dependence of transesterification, offering insights for the design of vitrimers for various applications.[31]

12. A catalyst-free vitrimer system featuring two competing bond exchange mechanisms was presented by Marc Guerre. Each mechanism was found to operate under different temperature conditions, resulting in a unique dual-viscosity profile: a gradual decrease at lower temperatures followed by a sharp drop at higher temperatures. A novel strategy for tuning and designing the rheological behavior of vitrimers for precise processing applications was provided by this discovery.[32]

13. In order to create a tertiary amine structure, Su et al. selected secondary amines as a raw material with varying structures and chain lengths to react with the same epoxy resin. The trans-esterification of this epoxy resin vitrimer was also catalysed by it. Since there is only one active hydrogen atom on its N atom, the reaction with epoxy resin is straightforward, making it simple to observe and evaluate throughout the experiment. An epoxy resin with a tertiary amine structure (ETA) was produced by the pre-reaction products of secondary amine and excess epoxy resin. A tertiary amine promoter (TAP) was produced by the pre-reaction products of secondary amine and comparable epoxy resin. For trans-esterification, they served as the source of catalytic activity, respectively.[33]

14. The covalent adaptive network in the Styrene Isoprene Styrene (SIS) elastomer is constructed by Jiang et al. They chose the dynamic boron-oxygen bond for their network. This material was created via a reactive process method, as opposed to a conventional solution method. Swelling studies, FT-IR, and stress relaxation tests were performed to quantify the crosslink density; this also provided insight into the dynamics of the -B-O bond exchange. The produced SIS vitrimeric elastomer exhibits significantly increased

lap-shear strength, mechanical strength, elastic recovery, and high creep resistance. The industry finds good use for the SIS vitrimeric elastomer as a high-performance green adhesive because it is reprocessable and self-healing.[34]

15. Taynton et al. established a network utilizing a difunctional aldehyde along with di- and trivalent amines. The substances were simply blended in an organic solvent, and the solvent evaporated once the reaction concluded. FT-IR analysis was employed to verify the formation of imines and the depletion of aldehydes. Glass transition temperature (Tg) was measured at 56 °C, and the Young's modulus at ambient temperature was found to be 1 GPa. The thermo-mechanical characteristics indicated that the material could relax more rapidly with an increase in temperature. At 80 °C, 90% of the stress was alleviated within 30 minutes, whereas at 25 °C, this relaxation would take 480 days.[35]

16.McCarthy et al. highlighted the significance of siloxane groups in the addition or removal of silanols and silanolate. They also showed that polydimethylsiloxane (PDMS) networks can achieve quantitative healing. These networks provide stress relaxation. Below 130 °C, the silanolate anion facilitates rapid exchange reactions, but they can be decomposed through thermal treatment at 150 °C, converting the living polymer into a permanent elastomer. Although the vitrimeric characteristics of these 'living' poly-siloxane networks still need investigation, thermal degradation appears to be a critical issue in established systems. The associative nature of the covalent bond exchange reaction should enable the development of new materials based.[36]

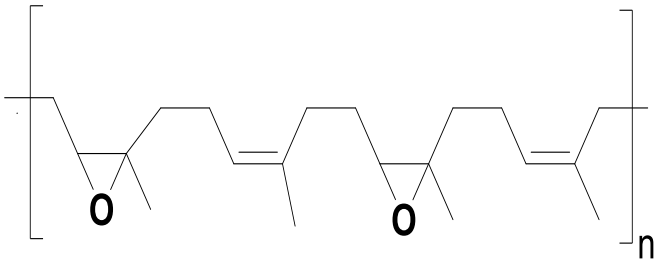
CHAPTER 3

EXPEERIMENTAL: MATERIALS AND CHARACTERIZATION

3.1 MATERIALS:

3.1.1 Epoxidized Natural Rubber:

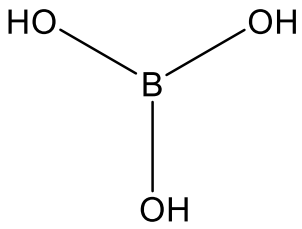
Epoxidized Natural Rubber (ENR) is a type of manufactured rubber derived from natural rubber. ENR is created by introducing epoxide groups into the polymer chain through chemical modification of natural rubber latex. Depending on the content of epoxide groups there are two types of ENR, one is ENR25 which contain 25 mol % epoxide group, and another is ENR50 which contain 50 mol % epoxide group on the cis 1,4-isoprene group. ENR50 have some unique properties like high elasticity, low heat buildup, gas permeability and high oil resistance. This alteration in the content of epoxy group modifies its properties, making it suitable for various modern applications. The increment in polarity because of epoxy group and gluing properties make ENR suitable for adhesives and sealants used in construction, automotive, 3D printing, Textiles and many other industrial applications. It is most commonly used in tire industry.[37]



ENR 50

3.1.2 Boric Acid:

It is a white crystalline solid at room temperature, known as orthoboric acid and weak monobasic Lewis's acid for its mild acidity and antiseptic properties.[38] Boric acid is widely used as an antiseptic for the treatment of minor cuts and burns. The overall molecular geometry of boric acid is trigonal planar. Boric acid is an ecofriendly, less expensive, easily available and non-hazardous chemical having three hydroxyl groups on the Boron atom.



Boric acid structure

3.1.3 Zinc Acetate:

Zinc acetate is a chemical compound with the formula $Zn(CH_3COO)_2$. It is a white crystalline solid with 219.50 g/mol (dihydrate), 183.48 g/mol (anhydrous) molar mass. It decomposes at 237°C (dihydrate loses water at 100°C) temperature. Its molecular shape is tetrahedral and coordination geometry is octahedral (dihydrate).

3.2 EXPERIMENTAL:

3.2.1 Preparation of sample:

First, ENR 50 was masticated in the two-roll mill for 2 mins at room temperature with rotor speed of 40 rpm. After some time, boric acid was added, after the complete mixing of boric acid, zinc acetate was added as a catalyst. A constant speed and gap were maintained between the rolls of two roll mill. The rubber mixture was then cured in 2 mm sheet by compressing hot molding machine under 10 MPa pressure at 160 ºC for respective cure time. Boric acid concentration varies from 1.5 to 3.5 phr for every 50 g of rubber sample.

3.3 CHARACTERIZATION:

3.3.1 Curing Study:

Curing properties of a composite were found employing Moving Dia Rheometer (MDR Xgen 100) at 160 ºC, for 60 min. The uncured material was positioned in a rheometer frequency 1.7 Hz at that point torque produced was measured against the time. The ideal cure time (t90) was obtained from the time-torque curve. At that point all the samples were cured corresponding to their cure time (t90) employing a compression molding machine. The formed rubber sheets are utilized for advanced characterization.

3.3.2 FTIR (Fourier Transform Infrared Spectroscopy Study):

FTIR was used to determine the functional group present in material, using an IR-Afnity-1 spectrometer (Shimadzu). Samples were obtained directly on the Zinc Selenide (Zn-Se) constricted add up to reflectance (ATR) crystal's surface analyzed in the 4000-400 cm^{-1} frequency range, with a scanning of 40 and an ATR resolution of 4 cm^{-1}.

3.3.3 Solid Nuclear Magnetic Spectroscopy (NMR)

Solid-state ^{13}C and B^{11} nuclear magnetic resonance (NMR) spectrum was recorded using ECX400 (JEOL, Tokyo, Japan) at the 400 MHz.[39]

3.3.4 Dynamic Mechanical Analysis (DMA):

Dynamic mechanical Analysis was employed to study about the viscoelastic properties of ENR-BA based composites through temperature sweep tests (-80 ºC to 80 ºC) at 10HZ.

3.3.5 Differential Scanning Calorimetry (DSC):

DSC study of rubber material was carried out with DSC 204 F1 (NETZSCH, Germany) instrument under heating rate of 10ºC per minute and nitrogen flow rate of 40 ml per min. 10-15 mg of fabric typified in an aluminum container with penetrated top. The container was set into the gadget at room temperature and warmed to 200ºC.

3.3.6 Mechanical Strength study:

Stress-strain behavior was studied by employing a Tinus Olsen universal Testing Machine (Demonstrate H10KT) prepared with a 500 N stack cell, in understanding with ISO 527-5A. Dumbbell-shaped specimen of dimension 75 mm (add up to length), 25 mm (gage length), 4 mm (width), and 2 mm (thickness) were utilized. Each detailing was tried three times to guarantee reproducibility.

3.3.7 Swelling and Crosslink Density:

Swelling Study was done to measure the degree of crosslinking of the cured rubber sheets. Hot pressed ENR-BA composite and pure ENR samples were swelled in the toluene solvent at room temperature and hold for seven days to check the crosslink density into matrix. Toluene was supplanted each 24 hours. The cross-link density (ve) was calculated using the Flory-Rehner equation.

3.3.8 Recycling Test:

To assess recyclability, cured rubber sheets were cut into small parts and thermally bonded at 130 °C beneath a pressure of 10 MPa for 30 minutes to make a uniform sheet. The tensile properties of reused rubber material were compared with those of the initial examples to decide the recycling proficiency.

3.3.9 Scanning Electron Microscopy (SEM):

SEM characterization is used to investigate the surface morphology of ENR-BA matrix, using a JEOL 6380A electron microscope with an accelerating voltage of 5` kV. Images were captured at magnifications 100× to assess surface morphology of composite

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Results and Discussions:

The ENR-BA composites are synthesized with varying concentrations of boric acid in the ENR matrix assisted by zinc acetic as a catalyst. This is done to illustrate the impact of catalysts in organizing engineering and functional performance. A study is conducted to evaluate the mechanical and dynamic mechanical properties of the elastomeric materials. Characterization was performed utilizing Fourier-transform infrared spectroscopy (FTIR) to affirm the arrangement of boronic ester linkages, whereas thermogravimetric examination (TGA) and differential scanning calorimetry (DSC) are utilized to understand the glass transition behavior. Mechanical properties are analysed through tensile testing and dynamic mechanical analysis (DMA), giving understanding into the versatility and modulus properties. Besides, the exchange between dynamic covalent bonds approves recyclability. Results show the structure-property connections and execution benefits of dynamically crosslinked ENR composites.

Table 1: Formulation of ENR composites

Sample code	ENR-50 (phr)	Boric acid (phr)	Zinc acetate (phr)
E-1.5BA-0.5Zn(OAc)$_2$	50	1.5	0.5
E-2.5BA-0.5Zn(OAc)$_2$	50	2.5	0.5
E-3.5BA-0.5Zn(OAc)$_2$	50	3.5	0.5

(phr : parts per hundred rubber)

4.1.1 Curing Study:

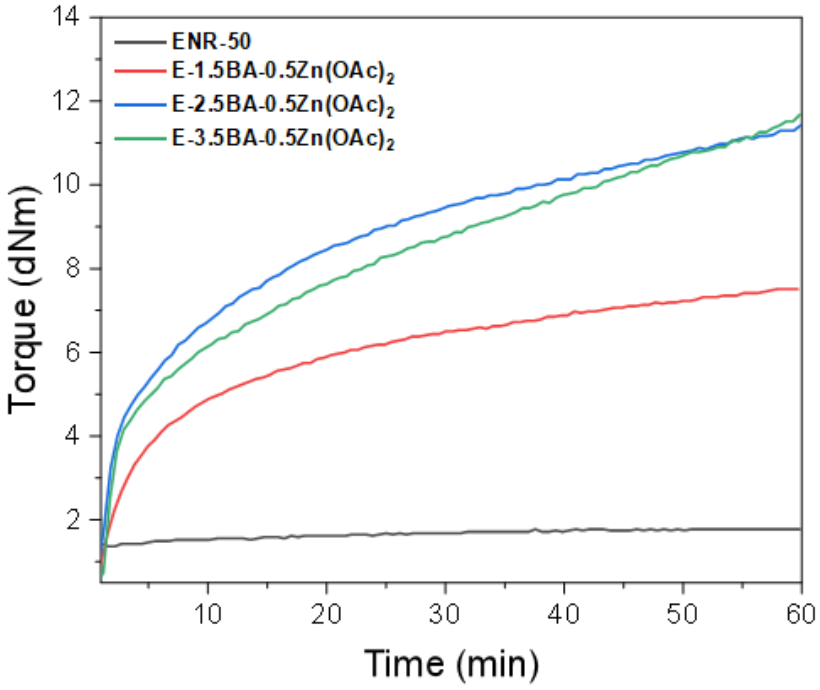


Fig 1. Rheometric curves of ENR-BA composite

Table:2 Rheometric parameters derived from the rheometric curves

Sample code	Maximum Torque (dNm) (T_{max})	Minimum Torque (dNm) (T_{min})	Cure Time (t_{90}) (min.)
ENR50	1.78	1.09	-
E-1.5BA-0.5Zn (OAc)$_2$	7.57	0.70	38.92
E-2.5BA-0.5Zn (OAc)$_2$	11.43	0.59	43.92
E-3.5BA-0.5Zn (OAc)$_2$	11.71	0.44	48.54

The curing properties of ENR-50 composites with boric acid as a crosslinker are examined through rheometric study, pointing to highest torque values as a degree of crosslink density (**Fig. 1 and Table 2**). The result is an increase in the highest rheometric torque with the consolidation of boric acid, which shows an increase in crosslinking inside the rubber matrix. This improvement causes the chemical reaction between the

epoxy reaction in ENR-50 and boric acid, assisted by zinc acetic as a catalyst. The observed increment in torque proposes the formation of a denser crosslinked network, which contributes to making strides of mechanical property. As the boric acid concentration increases, the crosslinking density and the torque values rise accordingly, highlighting the role of boric acid in reinforcing the matrix.[40]

4.1.2 Fourier Transform Infrared Spectroscopy (FTIR):

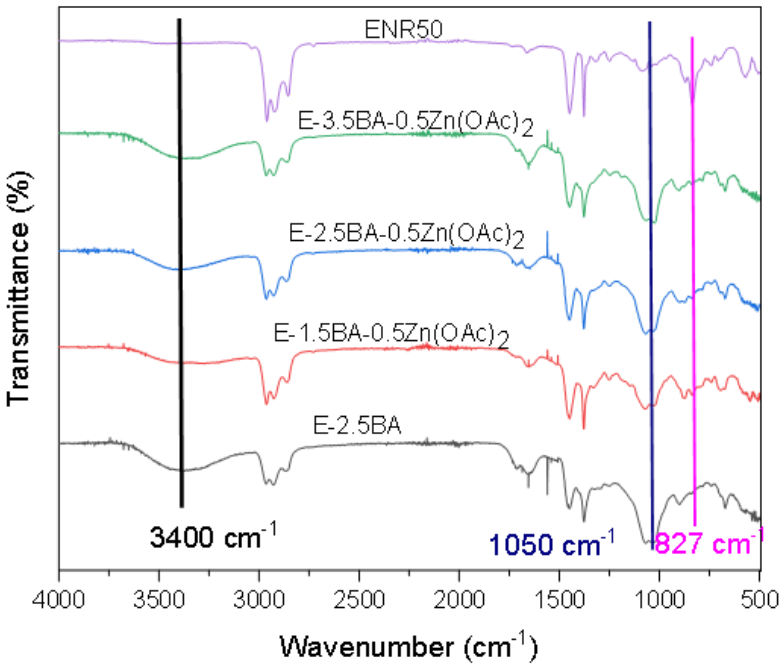


Fig 2: FTIR spectra of ENR-BA composites

The formation of dynamic covalent crosslinks in ENR50 composites crosslinked with boric acid was confirmed through Fourier Transform Infrared (FTIR) spectroscopy and solid-state NMR spectroscopy (^{11}B and ^{13}C). FTIR spectra provides critical insights into the chemical changes occurring during crosslinking. A prominent absorption band at 827 cm^{-1}, attributed to the C–O–C stretching vibration of epoxy groups in neat ENR50, is observed that decrease in intensity after the incorporation of boric acid. This decrease indicates the consumption of epoxy functionalities during the esterification reaction. Simultaneously, a new absorption peak, emerged at 1050 cm^{-1} is characteristic of B–O–

C stretching, confirming the formation of boronic ester linkages. Additionally, a broad peak around 3400 cm^{-1} corresponding to O–H stretching is noted, suggesting the presence of hydroxyl groups. These may result from unreacted hydroxyl functionalities or ring-opening reactions of the epoxy groups. The presence of hydroxyl groups further implies the possibility of hydrogen bonding within the matrix, which may enhance the mechanical integrity and damping behavior of the elastomer.[41]

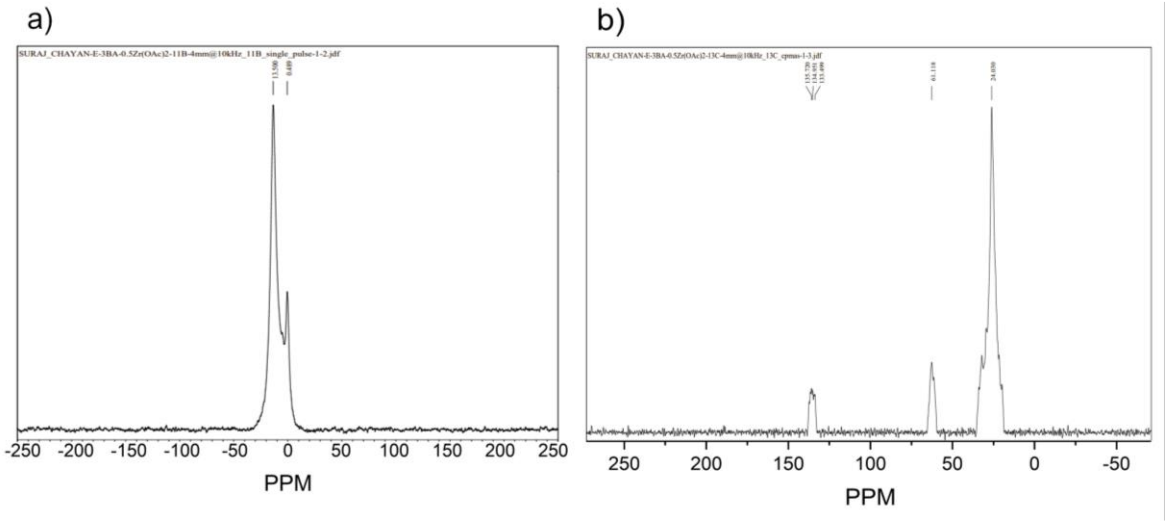


Fig: 3 Solid state NMR: a.) ^{11}B NMR of E3.5BA-0.5Zn(OAc)$_2$ b.) ^{13}C NMR of E3.5BA-0.5Zn(OAc)$_2$ of ENR50-BA

Further evidence in favour of crosslinking provided by solid-state ^{11}B & ^{13}C NMR spectroscopy. A sharp resonance at 13.50 ppm confirms the presence of tetrahedral boronate ester units (BO_4^{3-}), while a smaller peak at 0.489 ppm attributes to coupling between boron and nearby protons, suggesting interactions with hydroxyl or ring-opened groups in the matrix. Complementary ^{13}C NMR spectra exhibits peaks at 24 ppm for methyl carbons for both epoxidized and unmodified segments, 61 ppm for hydroxylated carbons, and a range between 133–136 ppm corresponding to methine and quaternary carbons of epoxy and olefinic groups.

These spectral observations validate the crosslinking mechanism between ENR and boric acid, demonstrating the formation of a dynamic network through B–O–C bonds. These reversible covalent linkages enhance the mechanical strength and thermal stability of the composite while enabling recyclability and reprocessability. The structural findings are well-aligned with the thermal, mechanical, and viscoelastic

properties discussed in other sections and establish boric acid as a highly effective dynamic crosslinker for vitrimeric elastomer systems.[42]

4.1.3 Thermogravimetry Analysis:

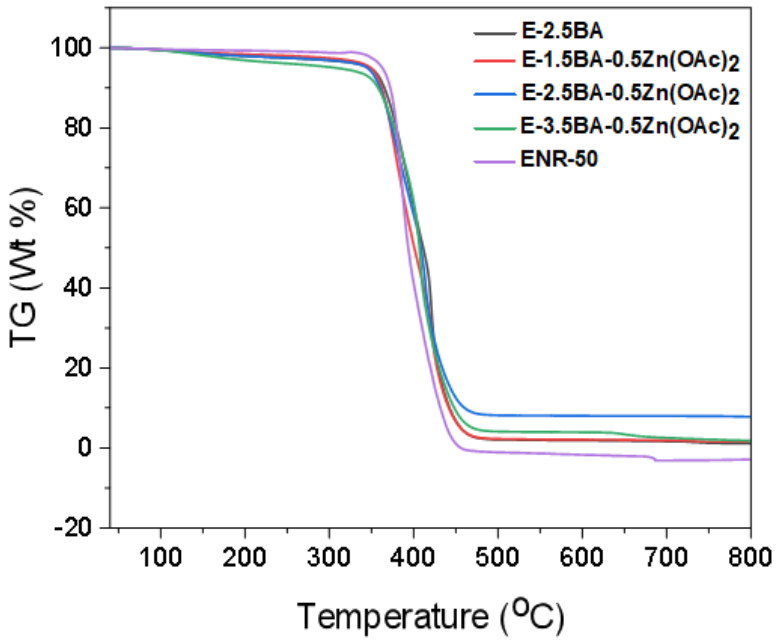


Fig 4: TGA curves of ENR50-BA Composites

Table:3 TGA parameters derived from the thermogravimetric curves

Sample code	ENR50	E-2.5BA	E-1.5BA-0.5Zn $(OAc)_2$	E-2.5BA-0.5Zn $(OAc)_2$	E-3.5BA-0.5Zn $(OAc)_2$
On set temp.	373.0	399.4	384.1	385.2	389.2
Mid-set temp.	394.2	412.7	401.6	406.8	407.3
End set temp.	412.9	432.6	436.2	431.1	425.0

Thermogravimetric study (TGA) is conducted to assess the thermal stability and decay of ENR-50 composites. The onset temperature, which corresponds to the start of substantial thermal decay, ranges from 384.1°C to 399.4°C (**Table 3 & figure 4**). Among all the samples, the E-2.5BA composite illustrates the most elevated onset

temperature at 399.4°C, signifying its ideal starting thermal stability. The addition of zinc acetate in the matrix decreases the onset temperature of other samples, due to its catalytic impact on the degradation process. A comparative trend observed within the midpoint temperature indicates the temperature at which 50% weight loss happens. The E-1.5BA sample displays the most elevated midpoint temperature of 412.7°C, whereas composites with zinc acetate shows slightly lower values, such as 406.8°C for E-2.5BA-0.5Zn $(OAc)_2$ and 407.3°C for E-3.5BA-0.5Zn $(OAc)_2$. These variations infer that zinc acetate has an impact on the thermal degradation.[43]

4.1.4 Differential Scanning Calorimeter (DSC) data analysis:

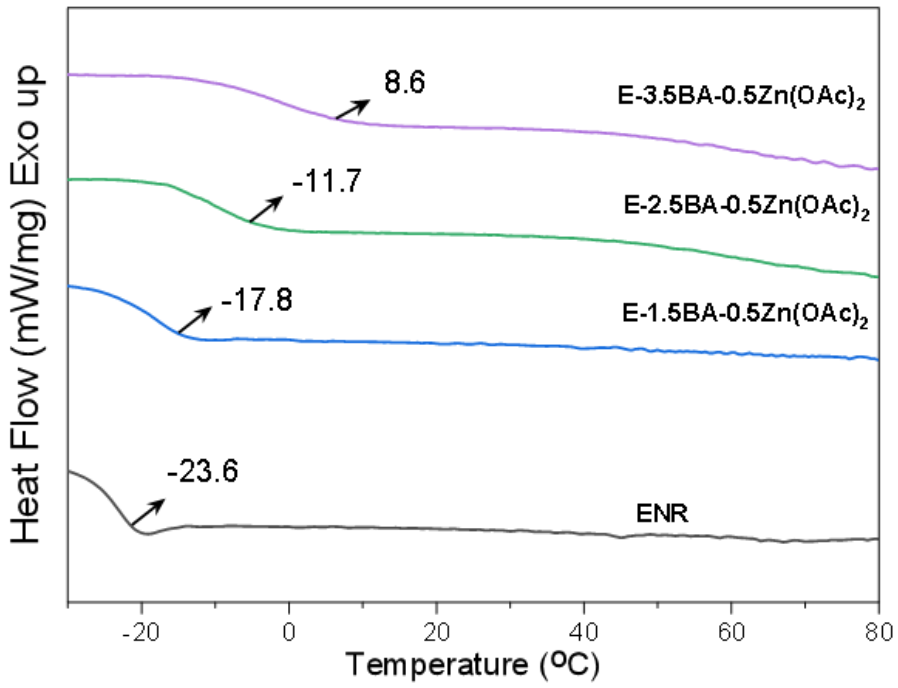


Fig 5: DSC curves of ENR50-BA Composites

The thermal behavior of ENR-50 composites with changing concentrations of boric acid is investigated using Differential Scanning Calorimetry (DSC). The investigation centered on the glass transition temperature (Tg), a key parameter reflecting the material's thermal stability and adaptability. The results illustrate a marked increment in Tg with increasing content of boric acid: Pure ENR-50 has Tg at -23.6°C, on addition of 1 phr boric acid Tg increases to -17.8°C, further increasing till 7 phr boric acid- Tg becomes 8.6°C. This dynamic increment in Tg demonstrates that the

incorporation of boric acid upgrades the crosslink density of the ENR-50 framework. The arrangement of bonds between boric acid and the epoxy groups in ENR-50 limits the atomic properties inside the rubber network, driving to stiffer and thermally more steady composites.[44]

4.1.5 Stress Strain Analysis:

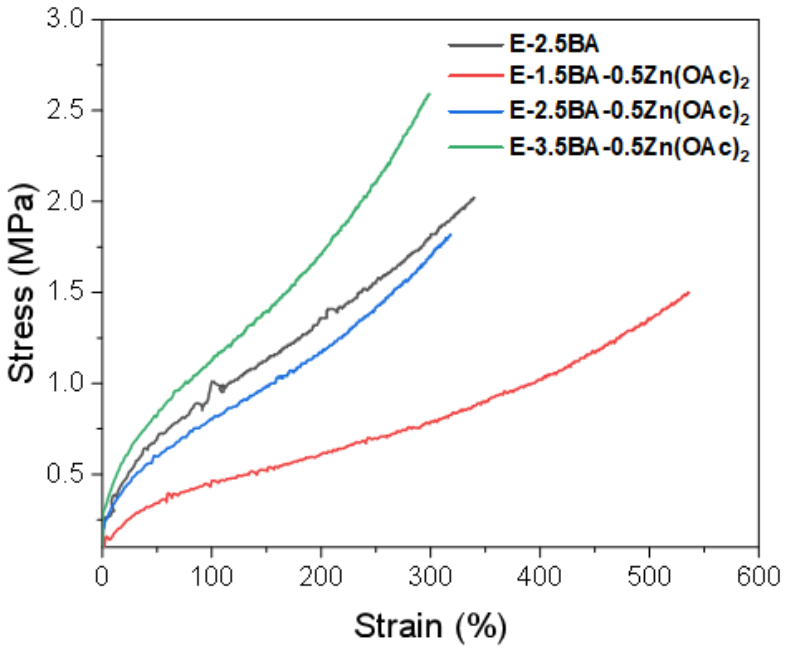


Fig 6: Stress Strain curves of ENR50-BA composites

Stress-strain investigation gives important knowledge on the mechanical performance of ENR-50 composites crosslinked with boric acid. It illustrates that the tensile strength of the composites increases with higher boric acid content. For the E-1.5BA-0.5Zn $(OAc)_2$ sample, the tensile strength is 1.50 MPa, which becomes 1.82 MPa for E-2.5BA-0.5Zn $(OAc)_2$ and a maximum of 2.59 MPa for E-3.5BA-0.5Zn$(OAc)_2$. This observation highlights the viability of boric acid in forming dynamic covalent bonds, with subsequent reinforcing the rubber network. In general, a reverse relationship is observed between tensile strength and prolongation at break. The stretching decreases from 569% for E-1.5BA-0.5Zn $(OAc)_2$ to 338% for E-2.5BA- 0.5Zn $(OAc)_2$ and 319% for E-3.5BA-0.5Zn $(OAc)_2$ (**figure 6**). This decrease in elongation is demonstrative of an

enhanced stiffness inside the composite, attributable to enhanced crosslink density, which in turn restricts molecular mobility and adaptability. This study hence illustrates the tunability of mechanical properties in ENR-50 composites by varying boric acid substance, providing a pathway for designing materials tailored to specific industrial needs.[45]

4.1.6 Dynamic mechanical analysis (DMA):

The viscoelastic behaviour and vibration damping efficiency of ENR-BA composites is analysed by Dynamic mechanical analysis (DMA) to investigate the viscoelasticity with varying boric acid content and zinc acetate catalyst. The temperature-dependent storage modulus (E′) and damping factors (tan δ) are displayed (**figure 7**). The storage modulus (E′) presents a degree of the material's elastic response and is demonstrative of the stiffness of the crosslinked rubber network. As illustrated in **Figure 7**, all samples show a characteristic thermorheological shift from a glassy state at low temperatures to a rubbery level at higher temperatures. A striking perception is the significant diminish in storage modulus (E′) with increasing temperature. This finding affirms the temperature-sensitive viscoelastic behavior, which is characteristic of an elastomer.

The E-3.5BA-0.5Zn $(OAc)_2$ composite displays the highest storage modulus over the temperature range, indicating a denser crosslinked network. This phenomenon can be credited to the higher concentration of boric acid, which facilitates the dynamic boronic ester linkages with the epoxy groups of the ENR-50. While the E-1.5BA-0.5Zn $(OAc)_2$ sample exhibits the least E′, reflecting a more adaptable network with diminished stiffness due to a lower crosslink density. These perceptions affirm that increase in the boric acid content increases the stiffness and structural integrity of the material by constraining the versatility of the polymer chains.

The damping factor (tan δ) may be a basic pointer of a material's capacity to disseminate vibrational energy. As illustrated in **Figure 7**, all samples display a distinct tan δ peak corresponding to the Tg. The E-1.5BA-0.5Zn $(OAc)_2$ sample illustrates the most elevated tan δ peak (~1.75 at 10°C), demonstrating its predominant vibration damping performance. This improved damping capacity can be credited to an adjusted

network design, which favors adequate chain portability. As the boric acid content increased to 7 phr, tan δ peak diminished (~0.98 for E-3.5BA-0.5Zn(OAc)2), and the Tg moves to ~18°C, demonstrating decreased damping due to a more obliged polymer matrix. In contrast, the E-2.5BA composite, arranged without zinc acetate, shows a tan δ value a) .3, affirming the significant role of catalytic activation in optimizing network dynamics. These perceptions are reliable with earlier considerations that present a trade-off between stiffness and damping in powerfully crosslinked systems. It is important to note that higher crosslink density improves mechanical quality but limits energy dissipation, whereas direct crosslinking favors prevalent damping behavior.[46]

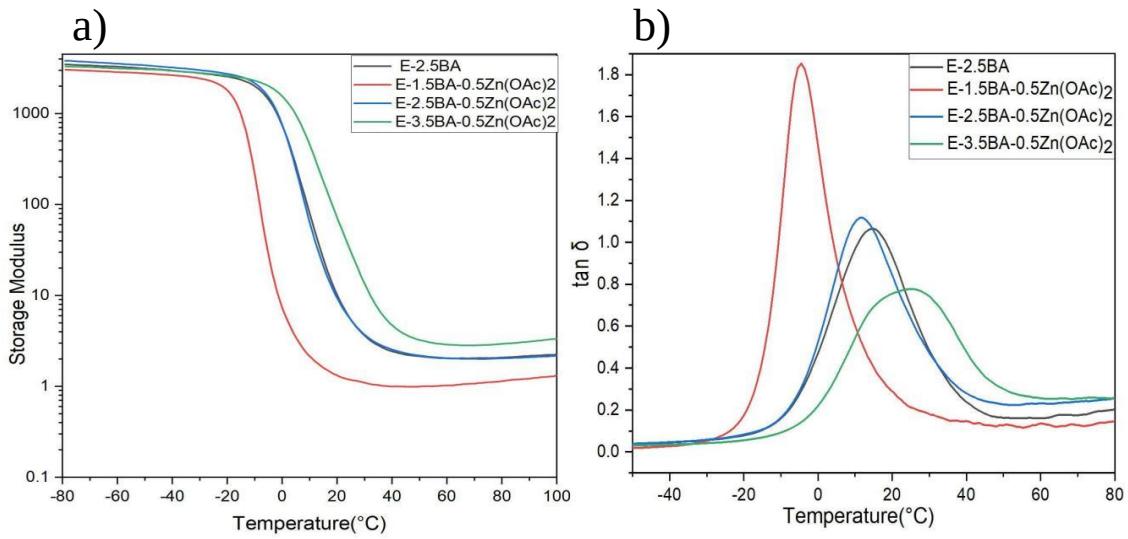


Fig 7: DMA curves a) Storage modulus vs Temperature b) tan δ vs Temperature of ENR50-BA composites

Table 4: DMA parameters of the ENR-BA composites

Sample Code	Tg (°C)	tan δ max
E-2.5BA	~12	~1.30
E-1.5BA-0.5Zn(OAc)$_2$	~10	~1.75
E-2.5BA-0.5Zn(OAc)$_2$	~15	~1.35
E-3.5BA-0.5Zn(OAc)$_2$	~18	~0.98

The result demonstrates that E-1.5BA-0.5Zn $(OAc)_2$ illustrates ideal performance, showing adjusted combination of moderate stiffness and uncommon damping capacity. This can be appropriate for vibration control applications such as adaptable isolators and automotive bushings. On the other hand, E-3.5BA-0.5Zn$(OAc)_2$ illustrates ideal performance in mechanically demanding situations, where inflexibility is of the foremost need.

4.1.7 Swelling and Crosslink Density:

Swelling experiments are performed to analyze the crosslink density of the composites using toluene as solvent. ENR50 completely dissloves in toluene while the crosslinked ENR-BA composites only swell in toluene, maintaining its original shape. The crosslinking density of the composites increases as the concentration of boric acid increases in ENR matrix. This indicates that there is an increased interaction between hydroxyl group of boric acid and the epoxide group of ENR matrix in this direction. Crosslink density (ν) was calculated using the Flory–Rehner equation, which relates the degree of swelling to the number of elastically active chains per unit volume (**Table 5**).[47]

Table 5: **Cross-link density parameters of ENR-BA composites**

Sample Code	**Cross-link density**
E-2.5BA	$3.2*10^{-4}$
E-1.5BA-0.5Zn$(OAc)_2$	$5.7*10^{-4}$
E-2.5BA-0.5Zn$(OAc)_2$	$5.9*10^{-4}$
E-3.5BA-0.5Zn$(OAc)_2$	$6.1*10^{-4}$

4.1.8 Recycling Study

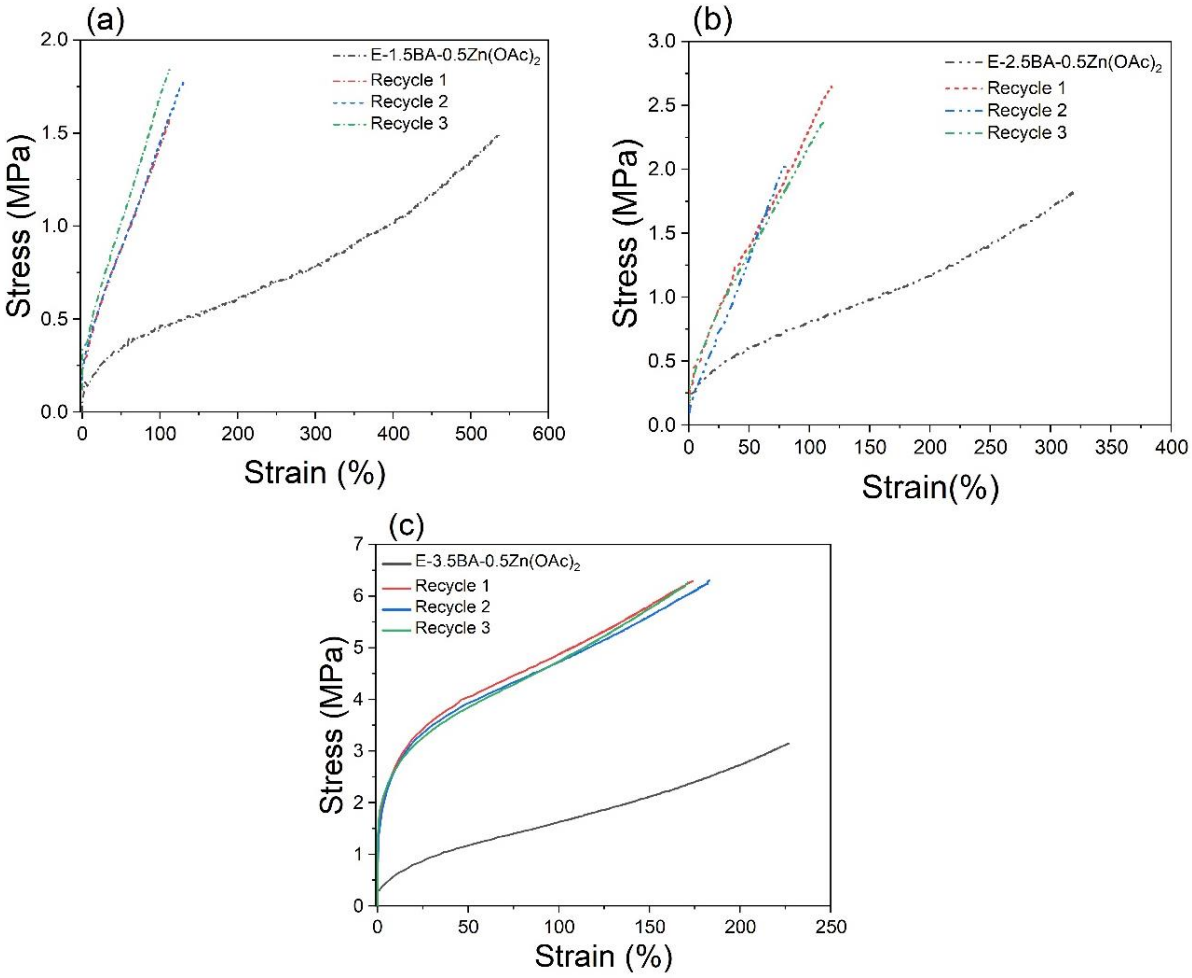


Figure 8 Recycling study of (a) E1.5BA-0.5Zn(OAc)$_2$, (b) E2.5BA-0.5Zn(OAc)$_2$ and (c) E3.5BA-0.5Zn(OAc)$_2$

The recycling performance of ENR50 composites is assessed after three thermal reprocessing cycles. As shown in Figure 7, all dynamically crosslinked samples retain a significant portion of their original tensile strength, confirming the effectiveness of boronic ester bonds in enabling network rearrangement and reprocessability.

E-1.5BA-0.5Zn(OAc)$_2$ exhibits the highest recycling efficiency, maintaining both tensile strength and elongation, due to its moderate crosslink density which allows effective bond exchange. In contrast, E-3.5BA-0.5Zn(OAc)$_2$, with its denser network, shows a greater decline in performance, likely due to restricted chain mobility during

reprocessing. Nevertheless, E-2.5BA-0.5Zn(OAc)$_2$ demonstrates balanced retention, highlighting it as an optimal formulation.[48]

4.1.9 Scanning Electron Microscopy (SEM):

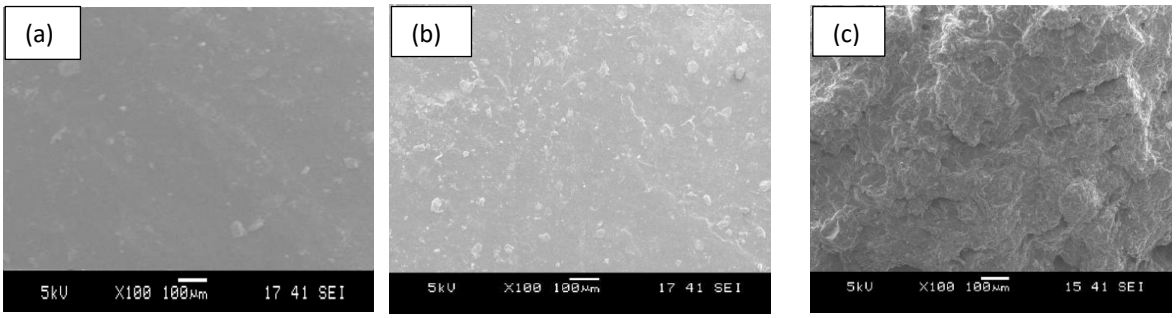


Fig. 9 SEM images of ENR50-BA composites

The surface morphology of ENR-BA composites is explored using Scanning Electron Microscopy (SEM) to assess the effect of zinc acetate and the effect of recycling on the microstructure of the dynamically crosslinked network. The micrographs are captured at 100× amplification and an accelerating voltage of 5 kV and shown in **Figure 9**. SEM picture of the (E-2.5BA) sample prepared without zinc acetate, the surface appears generally smooth and featureless. On the other hand, the sample (E-2.5BA-0.5Zn(OAc)$_2$) containing zinc acetate shows rougher surface texture. The increased roughness proposes improved crosslinking and phase partition, likely due to the formation of a dynamic covalent network encouraged by zinc acetate. The rough surface morphology is demonstrative of a more heterogeneous structure, characteristic of a dynamically crosslinked elastomer framework with micro-domains formed by reversible bonding interactions.

After three successive reusing cycles, the SEM picture of the reused sample with zinc acetate shows a wavy and layered morphology, proposing localized deformation and reorganization of the polymer chains. This geographical change highlights the material's capacity to experience thermo-mechanical recovery, enabled by the dynamic bond exchange responses characteristic to boronic ester chemistry.[49]

Chapter 5

Summary and conclusion

5.1 Summary

This study delivers a comprehensive assessment of boric acid as an innovative and efficient crosslinking agent for epoxidized natural rubber (ENR50) composites, offering a significant contribution to the field of advanced polymer materials. Through an experimental framework, the research explores the role of boric acid in modifying and enhancing the performance characteristics of ENR50, with particular focus on its chemical interactions, thermal behaviour, and mechanical properties. Fourier Transform Infrared spectroscopy (FTIR) serves as a crucial analytical tool to confirm the successful chemical integration of boric acid into the ENR50 matrix. The spectral evidence demonstrates the presence of newly formed B-O−C bonds alongside hydroxyl groups, indicating that boric acid actively participates in covalent bonding with the polymer chains. These findings suggest that boric acid does not act as a passive additive, but rather as a functional chemical crosslinker that enhances the internal network structure of the rubber composite.

Differential Scanning Calorimetry (DSC) analysis reveals a substantial increase in the glass transition temperature (T_g) with increasing concentrations of boric acid. This increment in T_g implies that the rubber matrix becomes stiffer and more thermally stable as the crosslinking density increases. The improved thermal resistance can be attributed to the restricted molecular mobility imparted by the boric acid-induced network.

The tensile strength of the composites is shown to improve progressively with the addition of boric acid, gives a peak value of 2.59 MPa for the composite formulation E-3.5BA-0.5Zn$(OAc)_2$. This mechanical improvement demonstrates the reinforcing effect of boric acid as a crosslinker that facilitates more robust intermolecular bonding, thereby enhancing load-bearing capacity and resistance to mechanical deformation. However, the study also reveals a decrease in elongation at break, indicating reduced flexibility and ductility.

On a broader scale, this research supports the growing demand for sustainable, high-performance rubber materials by promoting boric acid-a relatively abundant and low-cost compound as an alternative crosslinking agent to traditional sulfur-based systems. In addition to being environmentally friendly, boric acid’s ability to form dynamic bonds may also lend itself to reversible crosslinking, which could enable the

recycling or reprocessing of rubber products an increasingly important consideration in the era of circular materials engineering.

This work not only affirms the chemical and functional effectiveness of boric acid as a crosslinker in ENR50 composites but also opens new research pathways in the design of adaptable, high-performance rubber systems. Future studies may build upon these findings to explore synergistic effects with other crosslinkers, processing optimizations, or real-world application testing to fully realize the industrial potential of these advanced rubber materials.

5.2 Conclusion

This study demonstrates the effectiveness of boric acid as a crosslinker for ENR50 rubber composites, resulting in notable improvements in their chemical, thermal, and mechanical properties. FTIR analysis confirmed the successful incorporation of boric acid into the ENR50 matrix, with the formation of B−O−C bonds and hydroxyl groups indicating efficient chemical interactions and the establishment of dynamic covalent bonds during the curing process. Furthermore, the results of the thermal analysis, using the DSC technique, indicate a significant increase in the glass transition temperature (T_g) with higher boric acid contents, thus highlighting the enhanced stiffness and thermal stability of the composites. Mechanical testing further demonstrats that increasing boric acid content led to enhanced tensile strength, with the highest observed value of 2.59 MPa recorded for the E-3.5BA-0.5Zn$(OAc)_2$ composite. However, this enhancement in strength is accompanied by a reduction in elongation at break, reflecting a trade-off between mechanical strength and flexibility. The study emphasises the necessity of optimising the boric acid contents to achieve a balance between strength and elasticity, tailored to specific application requirements. This study thus establishes boric acid as an effective crosslinker and paves the way for innovative material designs aimed at meeting diverse industrial demands.

5.3 Future Scope

Vitrimers represent a significant and promising area of research within the larger field of materials science. They can endure high temperatures like thermosets while also being reprocessable like glass. This distinctive combination positions them as a potential option for recyclable thermoset composites. Elastomeric vitrimers will have a wide range of applications in the future, presenting various challenges and opportunities.

1. The topic of recyclability is highly important. One major advantage of vitrimer materials is their ability to be recycled. Traditionally, thermoset materials have demonstrated minimal potential for recycling due to the formation of irreversible chemical bonds during their curing process. In contrast, vitrimer materials can be recycled at high temperatures, offering an eco-friendlier alternative.

2. The development of vitrimer composites stands out as a significant area for future exploration in composite materials. These materials have the potential to transform the composite industry, which currently relies mainly on thermosets.

3. Investigating the mechanical properties of vitrimer composites is crucial. Another key focus is to compare the mechanical properties of elastic vitrimers with those of commercially available elastomers. Understanding these properties will support the design of vitrimers that may match or exceed the performance of existing materials.[50]

Elastomeric vitrimers hold great promises for the future, presenting numerous opportunities for research and development. The ability to integrate the advantages of thermosets and thermoplastics into a single material could lead to significant advancements in the field of materials science.

Chapter 6

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